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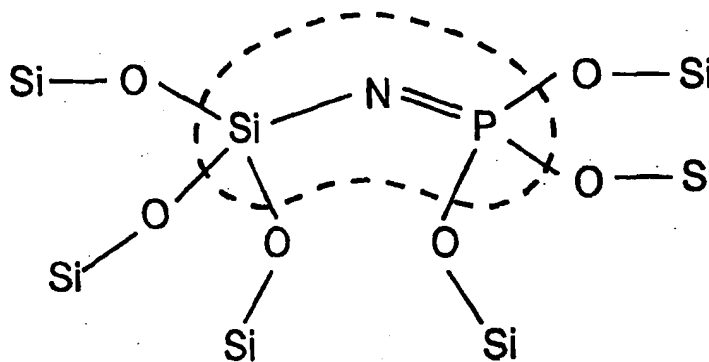
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(54) Title: MATERIAL WITH REDUCED OPTICAL ABSORPTION

## (57) Abstract.

A new material is proposed which is created by replacing in SiON silicon atoms partially by atoms of a penta- or hexavalent element, or by incorporating mono- or divalent metals interstitially. The thereby introduced electron-donating element is attracted to the nitrogen site and stabilizes it in its two fold coordinated, and therefore negatively charged form. In this form, the hydrogen affinity of the nitrogen atoms is reduced if not completely eliminated.

The achieved destabilization of hydrogen bound to nitrogen reduces the optical losses due to NH absorption.



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## MATERIAL WITH REDUCED OPTICAL ABSORPTION

The present invention relates to a solid material, more particular a material with a composition comprising silicon, a penta- and/or hexavalent and/or mono- and/or divalent element, oxygen and nitrogen, which material can be used as optical waveguide.

## 5 TECHNICAL FIELD AND BACKGROUND OF THE INVENTION

High-bandwidth communication relies increasingly on optical fibers and optical components for signal enhancement, signal-routing, adding and dropping information. An optical waveguide consists of a core made of some high-refractive index material and a cladding of a low-refractive-index material surrounding the core. In traditional optical-waveguide  
10 technology, the core and cladding of the waveguide are made of doped silica glass, where the refractive index contrast is achieved by a doping profile, for example using P-doping or Ge-doping. In order to fabricate optical components in a cost-effective way in mass production, it is desirable to fabricate them on silicon wafers. This results in planar waveguides. A review on planar waveguide technology is given in "Silica-based optical integrated circuits  
15 by Y.P.Li, C.H.Henry, IEE Proc.-Optoelectron. Vol. 143, No. 5, October 1996, pp. 263-280.

Because of space limitations in planar waveguide technology, smaller bending radii compared to traditional fiber technology are required. Smaller bending radii require a stronger guiding of the optical modes than in a straight waveguide or fiber. This is achieved  
20 by increasing the refractive index contrast between core and cladding as compared to the non-planar waveguide technology. US 5,500,031 gives an example for a method for increasing the index of refraction of a glassy material, wherein the material is treated with hydrogen under application of heat. However, limitations in the maximum achievable refractive-index-change by doping with P, Ge or other dopants and hence in the minimum attainable bending  
25 radius in the waveguide exist. A good compromise between the minimum bending radius and coupling losses to the standard fiber and the therefrom resulting necessary difference in the material composition between core and cladding can be obtained e.g. with an effective refractive-index contrast around 0.02.

In "A new curvature loss formula of Huygens-type for rib waveguides" by P.C.Kendall, M.S. Stern, P.N. Robson, in IEE Proc. Vol. 135, Pt.J, No.1, February 1988, p.11-16 the dependence of the bending radius and the refractive index contrast is reflected.

5 If the cladding is made of silica, i.e.  $\text{SiO}_2$ , which has a refractive index of 1.45, for the core a material with a refractive index near 1.51 is desired. Silicon oxinitride, i.e.  $\text{SiON}$ , can be chosen for the core, because its refractive index can be tuned over a wide range by changing the nitrogen concentration of the material. An example for use of  $\text{SiON}$  as waveguide is found in US 5,416,861.

10 In "Plasma-enhanced growth, composition and refractive index of silicon oxy-nitride films" by K.E. Mattsson in J. Appl. Phys. 77, No. 12, 15 June 1995, pp. 6616-6623, the variation of nitrogen in  $\text{SiON}$  for changing the refractive index is examined.

A particular feature of  $\text{SiO}_x\text{N}_y$ , resulting from a mixture of the components  $\text{SiO}_2$  and  $\text{Si}_3\text{N}_4$  is that it forms amorphous structures and that the components are miscible over the whole possible range. A typical composition of the waveguide core is  $\text{SiO}_{1.9}\text{N}_{0.08}$ .

15 A typical fabrication technique is to deposit silicon oxinitride using a PECVD process. The resulting material has however a large hydrogen concentration. Hydrogen is incorporated in the form of hydroxyl groups, Si-H groups and NH- and  $\text{NH}_2$ -fragments. These groups and fragments introduce additional absorption into the optical transmission characteristic of the silicon oxinitride. The first overtone of the NH-induced absorption band lies at 1505 nm and  
20 overlaps with the spectral window, which is used for optical signal transmission and which extends from 1540 nm to 1570 nm, hereinafter simply referred to as the optical transmission window. This window has been chosen for optical transmission due to the fact that silicate glass there has its lowest absorption and that erbium-doped optical amplifiers there have the range of most linear amplification as can be read upon in "Review of rare earth doped fibre  
25 lasers and amplifiers" by P.Urquhart, IEE Proc. Vol. 135, Pt. J, No. 6, December 1988, pp 385-407.

This absorption results in often unacceptably large losses for viable products. The NH concentration may even increase with time and humidity due to natural exchange with the surrounding medium. The hydrogen concentration and with it the resulting absorption losses  
30 are therefore currently reduced by a high-temperature annealing process as described in

"High contrast and low loss SiON optical waveguides by PECVD" by Offrein et al. in Proceedings 1996 Symposium of the IEEE/LEOS Benelux Chapter, Enschede, pp 290-293, which process consolidates the material, and reduces the hydrogen concentration by evaporating water and ammonia. The nitrogen atoms change their atomic neighborhood from two silicon atoms and one hydrogen atom to three silicon neighbors. The losses can however be reduced only to a certain extent, because longer annealing times are assumed to produce additional scattering centers, which is ascribed to crystallization or phase separation. Another approach to reduce the hydrogen content in SiON is described in "Low-Hydrogen Silicon Oxynitride Optical Fibers Prepared by SPCVD" by Dianov et al. in Journal of light-wave technology, vol. 13, No. 7, July 1995.

A negative side effect of the high-temperature annealing is the introduction of anisotropic stress.

The stress is caused by the difference in thermal expansion coefficients between the silicon substrate and the material of the waveguide. The stress correlates with the temperature difference between room temperature and the highest annealing temperature or a material-specific temperature close to its annealing point, whichever is lower. The stress gives rise to birefringence and polarization-dependent transmission characteristics. This waveguide behaviour is not desired for most of the applications while in US 478,142,4 a singlemode channel optical waveguide with a stress-induced birefringence control regions explicitly makes use of this effect. In "Temperature dependence of stresses in chemical vapor deposited vitreous films" by Shintani, Shojiro, Sugaki and Nakashima in J. Appl. Phys. 51(8), August 1980, pp 4197-4205, the dependence of the stress on various parameters, particularly the P content in phosphosilicate glass is investigated. Another investigation for P-doped silica is given in "Stress in chemical vapor-deposited SiO<sub>2</sub> and plasma-SiN<sub>x</sub> films on GaAs and Si" by C. Blaauw in J. Appl. Phys. 54(9), September 1983, pp 5064-5068.

The mechanism of substitution is e.g. known from zeolites, where the acidity of a zeolite, and therefore its catalytic activity, is engineered by controlling the aluminum content of the lattice, more about which can be found in "Studies on the acidity of Mordenite and ZSM-5. 2. Loss of Bronstedt Acidity by Dehydroxilation and Dealumination" by M.H.W. Sonnemans, C. den Heijer and M. Crocker in J. Phys. Chem. 1993, 97, pp 440-445.

An ion of an element behaves similar to a neutral atom of a different element, if the number of electrons is similar. In the case of zeolites, this implies that aluminum can replace a framework silicon atom, if it receives an additional electron. This causes an oxygen atom nearby to receive a positive charge, so that it, in turn, behaves like nitrogen. Nitrogen is trivalent, and requires an additional bond, which is supplied by a proton. From this argument it can be deduced that an aluminum atom in a position of a silicon atom attracts protons to a nearby oxygen atom, which is the structure of an acid site in zeolites.

A number of nitrides exist, where the substitution of SiO by PN and of NH to NM, wherein M is a metal, results in largely isostructural compounds.

- 10 Review articles on nitrides are "Crystal Chemistry of Inorganic Nitrides", by N.E. Brese and M.O'Keeffe in Structure and Bonding, 79, pp 307-378, Springer-Verlag, (1992); "Solid State Chemistry with Nonmetal Nitrides" by W. Schnick, Angew. Chemie, Int. Ed. Engl. 1993, 32, pp. 806-818; R. Niewa and H. Jacobs Chem. Rev. 96, 2053 (1996).

15 Silicate glass and PON are known materials. US 3,791,714 describes a method of producing glass for optical waveguides wherein deuterium is used instead of hydrogen to obtain glass having a low-hydroxyl-ion-content. The hydroxyl-ion normally present in glass produced in the presence of hydrogen is replaced by the deuterium-containing ion OD<sup>-</sup>. Absorption peaks normally caused by the presence of the hydroxyl ions are shifted to longer wavelengths at which the absorptions are not troublesome when the waveguide is used to transmit light in the band of approximately 7000 Å.

20 In "High-bandwidth, low-loss polymer fibres" by Yasuhiro Koike (ECOC '1992 Proceedings, Vol. 2, September 27 - October 1, 1992, Mo B1.1) deuteration is also used for polymer waveguides in order to reduce the attenuation.

#### OBJECT AND ADVANTAGES OF THE INVENTION

- 25 It is an object of the invention to replace silicon oxynitride by a material with a similar refractive index, which has a lower affinity to hydrogen, in particular in the form of NH bonds.

It is another object to provide such a material which has additionally a refractive index which is tunable over a certain range, particularly a range comparable to the range in which the

refractive index of silicon oxynitride is tunable and is hence larger in range than the conventional, doped silica materials.

It is another object to provide such a material which additionally is amorphous and compatible with current fabrication techniques.

- 5 It is another object to provide a material which has low loss in the spectral region from 1540 to 1570 nm.

It is another object to provide a material that allows tuning of the resulting stress in SiO<sub>2</sub>-based dielectric stacked layers.

- 10 It is another object to provide a material which can be annealed at lower temperatures than SiON in order to reduce thereby-caused undesirable side effects, such as stress and birefringence.

The above described problem is solved by a material having the features set forth in the independent claims.

- 15 When in the following it is referred to ASiON, a SiON structure which has an incorporated element, particularly a pentavalent or hexavalent element A, is meant. As pentavalent elements e.g. phosphorus or arsenic can be used. When in the following it is referred to MSiON, a SiON structure which has an incorporated element, particularly a monovalent or divalent element M, is meant. A mixed form, AMSiON can also be used. When in the following ASiON is mentioned, any of the forms ASiON, MSiON, AMSiON is meant.

- 20 The material according to independent claims 1 or 6 has the advantage that it has a reduced absorption in the transmission window between 1540 nm and 1570 nm. It furthermore has lower material stress.

- 25 Phosphorus and alkali metals are furthermore compatible with the currently used glass formation technology, as both are already used as network modifiers, e.g. for SiO<sub>2</sub>. A network modifier reduces the connectivity of the network of chemical bonds of a material. Thereby it softens the material, e.g. here glass, and allows to process it at lower temperatures. The role of phosphorus in SiO<sub>2</sub> differs significantly from that envisaged here in silicon oxynitride. In silicon oxynitride, phosphorus can change its chemical environment from three

bridges and one terminal oxygen to four bridges by undergoing a chemical reaction with nitrogen. A similar reaction does not take place in silica glasses.

Phosphorus is also compatible with the currently used silicon technology as it is commonly used as dopant in semiconducting devices. Phosphorus can for example be incorporated  
5 during a PECVD process using gaseous phosphine precursors.

The resulting material, namely a pentavalently or hexavalently substituted SiON, herein referred to as ASiON, is expected to be more resistant with respect to humidity than SiON. SiON readily reacts with water vapor. This reaction forms NH bridges and hydroxyl groups. Density-functional calculations of analog molecules show that the formation of PN pairs is  
10 energetically favored with respect to both NH bridges and nitrogen with three silicon neighbor atoms. Therefore, the reaction of water with PN bridges is endothermic, and consequently slower. The stability against water and humidity, is expected to be similar to that of silicate glass.

ASiON is based on the same structural principle as silicate. Therefore it is expected to form  
15 amorphous structures similar to silicate glasses.

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ASiON is expected to be thermodynamically and hence environmentally more stable than pure silicon oxynitride. The reaction to form nitrogen gas and silicon crystalites, as it is believed to take place at high temperatures in silicon nitride and silicon oxynitride, is slowed down. It is hence more stable concerning time, temperature and humidity.

20 The required annealing temperature required to reduce losses below a given level, is expected to be lower, respectively the annealing time required to reduce losses below a given level, is expected to be shorter than that of SiON since an exothermic reaction path is offered for the elimination of NH-bridges. This reaction path is envisaged as a pairing of a phosphorus atom and an NH-bridge, a proton transfer from the NH bridge to the onefold  
25 coordinated oxygen atom of the phosphorus. On one hand, the reaction rate of a NH bridge to a nitrogen coordinated to three silicon atoms, correlates with the concentration of available hydroxyl groups. On the other hand, also the undesired back-reaction correlates positively with the concentration of available hydroxyl groups and/or water molecules.

Since the hydroxyl groups anneal with each other forming water and oxygen bridges, the  
30 hydroxyl supply is reduced early in the annealing process. The reaction between a



- phosphorus atom and a NH bridge is, on the other hand, proportional to the density of phosphorus atoms not yet bound to nitrogen and only the undesired back-reaction is driven by the hydroxyl concentration. Thus, the reaction rate for eliminating NH bridges is expected to be accelerated compared to the phosphorus free silicon oxinitride. Because the
- 5 desired reaction is accelerated the annealing temperature and/or annealing time can be reduced. A reduction of annealing temperature and/or annealing time is desirable to avoid an eventual partial cristallization and/or phase separation of the material. Small crystals and inhomogeneities in the material composition introduce scattering losses if they grow to a certain size. Lower annealing temperatures result in lower stresses while cooling, which is
- 10 induced by the different thermal expansion coefficients between silicon and the waveguide material. Non-isotropic stresses result in a polarization-dependent refractive index, and hence cause optical birefringence. Optical birefringence makes the optical device sensitive to the state of polarization of incoming light. Because the latter is usually varying randomly in an optical fiber network this is a major issue.
- 15 A reduction of annealing temperature is advantageous, because it simplifies the production cycles and hence lowers device cost. Shorter annealing time simplifies the process and also increases processing speed, throughput and turnaround. Furthermore, a lower thermal treatment temperature will reduce the stress-induced birefringence.

20 The thermal expansion coefficient of ASiON is expected to be similar to the thermal expansion coefficient of SiO<sub>2</sub>.

Finally, the process of incorporating phosphorus is much cheaper than the process for deuterium, such that the process and the deriving material is cheaper than a deuterated waveguide.

#### SUMMARY OF THE INVENTION

- 25 A new material is proposed which is created by replacing silicon atoms in SiON partially by atoms of a pentavalent or hexavalent element, and/or by incorporating mono- or divalent metals interstitially. These electron-donating elements are attracted to the nitrogen site and stabilize it in its twofold coordinated, and therefore negatively charged form. In this form, the hydrogen affinity of the nitrogen atoms is reduced if not completely eliminated. Destabi-
- 30 lization of hydrogen bound to nitrogen reduces the optical losses due to NH absorption.

- The idea underlying the invention is that twofold bound nitrogen can be stabilized, if it receives an additional electron. Electrons can be donated to a silicate-based matrix in several ways. On the one hand, electro-positive metal atoms, can donate their electrons to the nitrogen. In this case, the metal ions play the role of the hydrogen atom, which they displace. On the other hand, a pentavalent element has a surplus of one electron, if it is incorporated on a tetrahedral site, such as a former silicon site, where only four electrons are consumed in bond-formation. The remaining electron can be transferred to the nitrogen atom, which is then stabilized in its twofold coordinated site. This effect can be understood by the principle of isoelectronic substitution. If an atom of a particular element receives an additional electron, it tends to behave as if it were an element with the atomic number increased by one. If an atom of a particular element loses an electron, it tends to behave as if it were an element with the atomic number decreased by one. Thus, a phosphorus atom behaves as a silicon atom if it donates its fifth valence electron to a nitrogen atom. The nitrogen atom that receives an electron behaves as if it were an oxygen atom.
- A pentavalent atom that could replace a silicon atom is phosphorus which leads to a molecule with the general formula  $\text{Si}_x\text{P}_y\text{O}_z\text{N}_d$ , herein also referred to as PSiON. The ideal composition of PSiON is  $\text{Si}_{1-z}\text{P}_z\text{O}_{2-z}\text{N}_z$ , wherein z can be tuned to obtain for example a desired refractive index, which correlates with the density of nitrogen atoms. A choice of  $z = 0$  yields silicate glass, while  $z = 1$  yields PON, both of which are known materials. The invention lies in between. A value approximately in the range  $0.05 < z < 0.07$  may be chosen for use in practice, because it is deemed a good compromise between achievable bending radius and incorporated losses. The pentavalent first-row atom, nitrogen, does not incorporate substitutionally in a fourfold coordinated site and is therefore not suitable. Phosphorus is the most likely candidate, and might also be replaced by arsenic. The heavy pentavalent elements, antimony and bismuth may also be used. The NH bridges are energetically less stable than PN bridges. The reaction energy of a conversion from a NH bridge to a PN bridge is estimated from density functional calculations to be approximately 0.8 eV. The reaction energy of a conversion from a NH bridge into a nitrogen atom that is coordinated to three silicon atoms under consumption of a hydroxyl group and under generation and subsequent elimination of a water molecule is approximately isoenergetic. Whereas in SiON there is no energetically favored reaction to remove NH bridges, PSiON offers such a pathway. Therefore nitrogen will be incorporated in the form of PN bridges, in contrast to a

high concentration of NH bridges. The absence of NH bridges results in smaller optical losses. The refractive index of  $\text{SiO}_2$  is only to a minor extent affected by the presence of phosphorus. This also expected for  $\text{PSiON}$ . It was shown that the refractive index of silicon oxinitride correlates much stronger with the density of N-Si bonds. The above holds also  
5 true for hexavalent elements.

The material can also be used as a gate isolator for MIS transistors. It serves for strain relaxation between the semiconductor-isolator interface by local bond saturation. The tunable refractive index can also be used in an advantageous manner for glasses with a higher refractive index than silica glass and a lower absorption than  $\text{SiON}$  in the infrared  
10 range. Optical sensors can also profit from the new material in that more complex sensor devices, or more sensitive and therefore longer devices can be built by exploiting the reduced optical losses. The improved resistance with respect to humidity, will render the device more reliable in an aggressive environment. Waveguides comprising the material are also more resistant with respect to radioactive radiation. A similar or even better perform-  
15 ance in this respect is anticipated for this material.

#### DESCRIPTION OF THE DRAWINGS

Examples of the invention are depicted in the drawings and described in detail below by way of example. It is shown in

Fig. 1a, a material fragment with a central structure of an oxygen-bridged silicon pair  
20 (Si-O-Si),

Fig. 1b, a material fragment with a central structure of an NH-bridged silicon pair (Si-NH-Si),

Fig. 1c, a material fragment with a central structure of a phosphorus atom coordinated only to oxygen (P-O) and linked via oxygen bridges to three silicon atoms,

25 Fig. 1d a material fragment of a nitrogen atom connected to three silicon atoms,

Fig. 1e, a material fragment with a central structure of a hydrogen-free nitrogen bridge (Si-N-P) connecting a phosphorus and a silicon atom,

Fig. 1f, a material fragment with a central structure of a hydrogen-free nitrogen bridge (Si-N-P) connecting two silicon atoms and coordinated to a sodium ion,

Fig. 2, a diagram showing three different states of PSiON and their inherent energetic value. (Energetics of Competing Reactions in PSiON)

- 5 All the figures are for sake of clarity not shown in real dimensions, nor are the relations between the dimensions shown in a realistic scale. The fragments represent a part of a network of a solid state material which can be imagined as a continuous repetition of the fragments combined accordingly. The central structures in the depicted fragments are surrounded by a dashed line in figs 1a to 1f.

10

## DETAILED DESCRIPTION OF THE INVENTION

In the following, the various exemplary embodiments of the invention are described.

- In figure 1a, a structure of an oxygen bridge in silica, (Si-O-Si), known in the prior art is shown. Two Si atoms are connected to each other via one oxygen atom. Furthermore, the Si atoms are each bound onefold to further oxygen atoms which are all again bound to further silicon atoms. The central point of interest is the oxygen bridge between the two Si atoms  
15 which is the main structural element of SiO<sub>2</sub>. Every silicon atom in SiO<sub>2</sub> is connected via four such bridges to four other silicon atoms. The oxygen bridge does not give rise to any absorption peak in the optical transmission window.

- In figure 1b, the respective structure of an NH bridge in silicon oxinitride, (Si-NH-Si) known in the prior art is shown. In contrast to fig. 1a, herein the oxygen atom between the silicon atoms is replaced by a pair made up of a nitrogen atom and a hydrogen atom. Since nitrogen is trivalent, it has a terminating coordination to the hydrogen atom. Nitrogen is used as dopant to influence and therewith tune the refractive index of the SiON material. Before this material is annealed or if the material is exposed to water or a humid ambient for a sufficiently long time, most of the nitrogen in silicon oxinitride is present in the form of the shown NH bridge. A network containing such NH bridges has an absorption peak near the optical transmission window.  
25

- In figure 1c, the structural element of a phosphorus atom incorporated as network modifier in a silica network (p-doped SiO<sub>2</sub>) is shown as known in the prior art. The phosphorus atom substitutes one silicon atom and hence is only fourfold bound in this position. As only four  
30 of its five electrons are consumed by bond formation, it has a negative charge to offer. This

electron is transferred to one of the oxygen atoms, which is then stabilized in its onefold coordinated state. The onefold coordinated oxygen atom can not serve as bridge to another silicon atom such that the connectivity of the network is reduced. The thereby achieved softening of the glass lowers its viscosity but has no direct influence on the hydrogen content in the glass matrix.

In figure 1d, the structural element of a nitrogen connected to three silicon atoms is shown as known in the prior art. This is the dominant structural element in  $\text{Si}_3\text{N}_4$  and it is the way nitrogen is present in fully annealed silicon oxinitride. Since no hydrogen is present no NH-induced absorption takes place. The NH bridges in non-annealed SiON can only be transformed into nitrogen connected to three silicon atoms by a high-temperature, long-time annealing process, which has the already mentioned detrimental side effects.

In figure 1e, the structural element of a PN bridge in in PSiON (Si-N-P) is depicted. The phosphorus atom substitutes a silicon atom in a NH bridge compared to SiON in fig. 1b. The phosphorus atom is connected with three oxygen bridges and one nitrogen bridge to four silicon neighbors. The surplus electron of the phosphorus has been transferred to the nitrogen atom of the nitrogen bridge. Hence, the nitrogen atom is no longer reactive towards hydrogen so that no hydrogen is present in the bridge. This will be described in more detail in connection with fig. 2. With other words, the pentavalent element phosphorus has a surplus of one electron, if it is incorporated on a tetrahedral site, here the former silicon site, where only four electrons are consumed in bond-formation. The remaining electron is transferred to the nitrogen atom, which is then stabilized in its twofold coordinated site.

In figure 2, the energetic diagram of PSiON is depicted. More precisely, the reaction energies of typical annealing processes are shown, as obtained from quantum mechanical calculations of molecular fragments. A starting conformation comprises two silicon atoms connected via a NH Bridge, a silicon atom bound to a hydroxyl group and a phosphorus atom coordinated to a onefold coordinated oxygen atom. The lines towards the enclosing circle represent chemical bonds of these structural fragments to the remaining network of this material. The fragments shown are the essential partners in the annealing reaction of NH bridges. The coordination of phosphorus as depicted in the starting conformation 10 corresponds to a way phosphorus can be incorporated in silica or SiON, and in which it would act as network modifier in SiON. The phosphorus atom is coordinated with one oxygen that is

coordinated only to the phosphorus atom, and to three further oxygen atoms that form bridges between the phosphorus atom and silicon atoms. Hydroxyl groups are often present in silicate glasses. They can be removed by a high-temperature annealing process. The NH bridge is the way most of the nitrogen is present in silicon oxinitride before a high-  
5 temperature annealing process. The NH bridge results in optical absorption in the signal transmission window.

While splitting off a water molecule, an approximately isoenergetic reaction can lead to a first conformation 11 which comprises a nitrogen atom bound to three silicon atoms and still the phosphorous atom coordinated to the oxygen atom. The reaction from the NH bridge to  
10 a nitrogen atom coordinated to three silicon atoms requires a hydroxyl group and produces a water molecule. The phosphorus atom does not take part in this reaction. The reaction from the starting conformation 10 to the first conformation 11 is the reaction that anneals the NH bridge in SiON. As no energy is produced, this reaction is driven only by the relative concentration of hydroxyl groups and NH bridges. The resulting undersupply of hydroxyl  
15 groups shifts the equilibrium concentration towards the form of the first conformation 11. However, as a hydroxyl group is required for the reaction, an undersupply of hydroxyl groups slows down simultaneously the reaction.

A second conformation 12 depicts the reaction product of the annealing reaction of the hydroxyl group. The phosphorus atom and the NH bridge do not take part in this reaction.  
20 The hydroxyl group pairs with another hydroxyl group, not drawn in the circle to an oxygen bridge and a water molecule. As only one hydroxyl group is drawn in the circle, only one-half of the reaction energy of 1.54 eV, namely 0.77 eV, can be counted for the exothermic reaction and only one half of an water molecule must be considered as reaction product. This reaction is the main annealing reaction in SiO<sub>2</sub> and SiON. This reaction depletes the  
25 concentration of hydroxyl groups in the early phase of the annealing process.

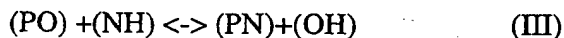
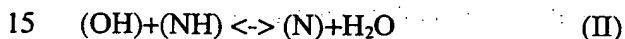
The resulting undersupply of hydroxyl groups shifts the equilibrium concentration of the reaction from the starting conformation 10 towards the first conformation 11 in the direction of nitrogen bound to three silicon atoms but also slows down the reaction speed, as hydroxyl groups are a prerequisite for the reaction from the starting conformation 10 to the first  
30 conformation 11.

Because of the slow final reaction from the starting conformation 10 to the first conformation 11, long annealing times and/or high annealing temperatures are required with the mentioned side effects, i.e crystallisation, birefringence etc.

5 A third conformation 13 depicts the reaction product between the phosphorus atom and the nitrogen atom, namely a hydrogen-free nitrogen bridge and an oxygen bridge, which results in an energy gain of 1.53 eV. This reaction is envisaged as pairing of the phosphorus, bound to a onefold coordinated oxygen and the NH bridge, a proton transfer from the NH bridge to the singly coordinated oxygen. This creates a hydroxyl group on phosphorus, that anneals with the available hydroxyl group of the silicon atom to a free water and an oxygen bridge.

10 Since the principally preferred direction of a chemical reaction is exothermic, hence from higher energy to lower energy, the preferred and automatically arising conformation of PSiON will be largely the third conformation 13.

The most-relevant reactions are



Here, (N) is a nitrogen atom coordinated to three silicon atoms, (NH) is an NH bridge, (OH) is a hydroxyl group, (PO) is an oxygen atom onefold coordinated to a phosphorus atom, (PN) is a hydrogen-free nitrogen bridge, (H<sub>2</sub>O) is molecular water and (O) is an oxygen  
20 bridge.

In this rate equation the reaction forming a PN bridge has been divided into a first step that forms the hydrogen-free nitrogen bridge and a hydroxyl group (III) and a second step which corresponds to the annealing of two hydroxyl groups (I) as shown in fig 2, particularly for the reaction from the starting conformation 10 to the second conformation 12. The equation  
25 (II) represents the reaction from the starting conformation 10 to the first conformation 11.

The rate equations for this set of reactions are

$$d[\text{OH}]/dt = -k_1[\text{OH}]^2 + k_2[\text{H}_2\text{O}][\text{O}] - d[\text{N}]/dt + d[\text{PN}]/dt$$

$$d[NH]/dt = -d[N]/dt - d[PN]/dt$$

$$d[N]/dt = k_3[NH][OH] - k_4[H_2O][N]$$

$$d[PN]/dt = k_5[NH][PO] - k_6[PN][OH]$$

$$d[PO]/dt = -d[PN]/dt$$

$$5 \quad d[O]/dt = k_1[OH]^2 - k_2[H_2O][O]$$

Here, [N] is the concentration of nitrogen atoms coordinated to three silicon atoms, [NH] is the concentration of NH bridges, [OH] is the concentration of hydroxyl groups, [PO] is the concentration of oxygen atoms onefold coordinated to a phosphorus atom, [PN] is the concentration of hydrogen-free nitrogen bridges, [H<sub>2</sub>O] is the concentration of molecular water and [O] is the concentration of oxygen bridges.

The coefficients  $k_1 - k_6$  are the rate constants for the corresponding reaction. They are given by the reaction-free enthalpy  $G_i$  by  $k_i = \exp(-G_i/(k_B T))$ . Neglecting entropy contributions they are estimated from the numbers in fig. 2 to  $k_2=k_1$ ;  $k_3=k_4$ ;  $k_5/k_6 = \exp(1.5eV/k_B T)$ .

The rate equation for the concentration of the hydrogen-free nitrogen bridges is

$$15 \quad d[NH]/dt = -k_5[NH][PO] - (k_3[NH] - k_6[PN])[OH] + k_4[N][H_2O]$$

In the limit of very low concentrations of hydroxyl groups, which implies a concentration of hydroxyl groups smaller than the concentration of PO groups, and low concentration of water only the first term dominates, which is the formation of hydrogen-free nitrogen bridges.

20 In contrast, the corresponding rate equation for silicon oxinitride

$$d[NH]/dt = -k_3[NH][OH] + k_4[N][H_2O]$$

slows down as the concentration of hydroxyl group reaches a low level.

The general composition of PSiON is  $Si_aP_zO_xN_yH_u$ , wherein  $a, x, z, y$  are numbers bigger than 0. The hydrogen content  $u$  may be zero or higher, depending on the efficiency of the dehydration achieved by the phosphorous. The hydrogen content  $u$  is often also omitted in the chemical formula so that it is  $Si_aP_zO_xN_y$ .



The preferred composition of PSiON is  $P_ySi_{(1-y)}O_{(2-y)}N_y$ . This material is isostructural to  $SiO_2$ . This results in a match to silica in that a similar working temperature, annealing temperature, thermal expansion coefficient, density etc. can be assumed. Some of the oxygen bridges of silica are replaced by PN bridges in PSiON. The quantity  $y$  can be tuned to obtain the  
5 desired value of refractive index.

This material can contain a certain amount  $u$  of hydrogen by adding a variable amount of  $H_2O$  resulting in a material of composition  $Si_{(1-y)}P_yO_{(2-y+0.5u)}N_yH_u$ . If the water reacts with silicon oxinitride, most of the hydrogen is bound to nitrogen forming NH bridges, which result in optical losses. In PSiON, the hydrogen will not bind preferentially to nitrogen, but  
10 will be present as hydroxyl groups bound to silicon atoms. Hydroxyl groups have an absorption band further away from the signal transmission window than NH bands. Correspondingly, the losses are smaller than in SiON. Furthermore, the hydroxyl groups react easier to water in an annealing process, so that the preferred composition is obtained faster and/or at lower annealing temperatures. The material may be overdoped or underdoped with phosphorus resulting in a composition of  $Si_{(1-y)}P_zO_{(2-3.5y+2.5z)}N_y$ , where the over- or underdoping  
15 concentration ( $z-y$ ) may be greater or smaller than zero. The surplus of phosphorus atoms is incorporated as in phosphorus-doped silica. Its role is then to soften the material and to accelerate the annealing processes. The role of the surplus phosphorus is hence that of a network modifier. As the surplus phosphorus does not interfere with the beneficial function  
20 of forming hydrogen-free nitrogen bridges, overdoping may be desired to speed up the annealing process. Underdoping with phosphorus will result in only a partial replacement of NH bridges by hydrogen-free N-bridges. Taking this modification together with the previous one results in a material of composition  $Si_{(1-y)}P_zO_{(2-3.5y+0.5u+2.5z)}N_yH_u$ .

Instead of a phosphorus, also any other pentavalent element which can replace a silicon atom  
25 except nitrogen can be used. It is conceivable that arsenic readily incorporates into the glass matrix and exhibits effects similar to phosphorus. The heavier pentavalent elements may not readily incorporate into the matrix or incorporate in a different way, so it may only partially serve the function of forming hydrogen-free nitrogen bridges.

Instead of a pentavalent element also a hexavalent element, hence an element from group 16,  
30 except oxygen can be used. This material donates two electrons instead of one to the system. The two electrons may only partially contribute to hydrogen-free nitrogen bridges,

and/or they partially result in singly coordinated oxygen. The role of the latter would be that of a network softener. Sulfur may hence be substituting a silicon in the Si-NH-Si bridge and simultaneously provide for a hydrogen-free bridge and a hydrogen-free oxygen.

The material can also be oxygen-deficient by a number of  $q$  oxygen atoms. Silica glasses,  
 5 silicon oxynitride and silicon nitride are often produced with less than the stoichiometric amount of oxygen or nitrogen respectively. This material exhibits some Si-Si bonds. Some of these bonds may be broken and saturated by hydrogen atoms. The presence of Si-Si bonds does not interfere with the desired formation of hydrogen-free nitrogen bridges. The Si-H bonds absorb at sufficiently low frequency and therefore have only little effect on the optical  
 10 absorption losses. Taking this modification together with the previous ones results in a material of composition  $\text{Si}_{(1-y)}\text{P}_z\text{O}_{(2-3.5y+0.5u+2.5z-q)}\text{N}_y\text{H}_{(u+p)}$ , wherein  $p$  is the concentration of hydrogen atoms bound to a silicon atom or an atom that substitutes a silicon atom. It can have a value between  $0 \leq p \leq 2q$ .

The effect of replacing silicon by phosphorus can be achieved also by adding a monovalent  
 15 element other than hydrogen to the material, as it is depicted in fig. 1f. The depicted fragment has essentially the same structure as the fragment of fig. 1b, but here the hydrogen atom is missing whereas a  $\text{Na}^+$  metal ion is present near the nitrogen site which is negatively charged with the electron donated by the sodium atom. A monovalent element is an element from group 1 or from group 11, e.g. a metal atom. The metal atom can incorporate intersti-  
 20 tially and may donate an electron to an N bridge which otherwise would have coordinated to a hydrogen atom, thus forming a hydrogen-free nitrogen bridge. The monovalent element thus functionally replaces the hydrogen atom. The electron-donating atom is attracted to the nitrogen site and stabilizes it in its twofold coordinated, and therefore negatively charged form. The optical absorption in the signal transmission window of the monovalent element is  
 25 substantially lower than the optical absorption of the NH bridge, because of the lower bond strength and its larger mass, so that the corresponding absorption in the signal transmission window is negligible. This material is referred to generally as SiONM, M being the monovalent element. The electro-positive atom of the monovalent element donates its electron to the nitrogen. In this case, the metal ion play the role of the hydrogen atom, which it  
 30 displaces.

Instead of a monovalent element any divalent element, i.e. from group 2 or group 12, can be used. This material donates two electrons instead of one to the system. The two electrons may only partially contribute to hydrogen-free nitrogen bridges, and/or they partially result in singly coordinated oxygen. Particularly for interstitial placing of the divalent element, each  
5 electron might contribute to a hydrogen-free bridge. The role of the second electron could also be that of a network softener. As an example, calcium can be used as network softener, and is expected to react also with PSiON, where it can contribute to formation of hydrogen-free nitrogen bridges. As such mono- and divalent materials Li, Be, Na, Mg, K and Ca are preferably suitable. The heavier elements can be used too but are more expensive.

- 10 The general composition of the material with the mono- or divalent element, can be given as  $\text{Si}_4\text{O}_x\text{N}_y\text{M}_v$ , wherein M is the monovalent or divalent metal incorporated interstitially into the matrix of SiON and x is a number bigger than 0, y is a number bigger than 0 and v is a number bigger than 0. The variable v should be chosen smaller than the maximum number before phase separation occurs. Phase separation is a natural limit which is defined as the  
15 mixture at which the material is separated into different phases and hence does no longer remain SiONM. When  $v = y$ , the material has the composition  $\text{Si}_4\text{O}_x\text{N}_y\text{M}_y$ . This choice ideally eliminates every existent NH bridge. It proves however useful to choose v bigger than y. The fact that not every metal atom will find its place where it can act as expected is then taken into account by this overdoping of the SiON material in order to get the desired  
20 number of effective interactions.

Present planar waveguides use a nitrogen composition of seven percent relative to the silicon concentration, in order to reach a compromise between bending radii and absorption losses. A higher refractive index would be beneficial if no absorption losses due to NH bridges would be introduced. Therefore the anticipated composition is that given above with a nitro-  
25 gen concentration of 0.05 mol nitrogen per mole of silicon and phosphorus atoms.

All the modifications of the PSiON material mentioned above can be combined. The material can furthermore be functionalized using additional elements as dopants. For example Er or other f-electron elements may be added to achieve an optical amplifier. The combination of substitutional pentavalent or hexavalent elements with monovalent or divalent elements leads  
30 to the material which has essentially the composition  $\text{Si}_4\text{O}_x\text{N}_y\text{A}_z\text{M}_u\text{H}_v$ , wherein  $a > 0$ ,  $x > 0$ ,  $y > 0$ ,  $v+z > 0$ ,  $u \geq 0$ . The atoms of the chemical element M and/or the atoms of the chemical

element A effect the transformation of the NH bridges present in SiON into hydrogen-free bridges when treating SiON with these elements, respectively an avoidance of NH bridges, when manufacturing the  $\text{Si}_x\text{O}_y\text{N}_z\text{A}_v\text{M}_w\text{H}_u$ .

5 The preferred value for the refractive index  $n$  is approximately at least 1.5. To achieve a substantial elimination of NH bridges, preferably it may be chosen that  $z+v>0.25y$ . If the cladding is made of silica, i.e.  $\text{SiO}_2$ , which has a refractive index of 1.45, it is therefore desirable to choose  $y>0.05(a+z)$  or  $a=1-y$ ,  $x=2-y$  and  $z+v=y$ , with  $z$  lying preferably between 0.04 and 0.08.

10 The invention's gist lies in the fact that in SiON instead of one or several Si-atoms the respective number of atoms of a different element is incorporated and/or atoms of a different element are added, such that at least one hydrogen-free nitrogen bridge occurs. Thereby an eventual annealing process can be driven at low temperatures, and offers a broad range of choosable annealing temperatures which leads to a resulting choice of remaining stress.

15 But also already annealed PSiON in the first conformation 11 can be treated according to the invention's concept such that the threefold bound nitrogen is transformed into a twofold coordinated nitrogen in a PSiON with hydrogen-free bridges.

Any material obtained by incorporating additional elements to the material composition described above is covered by the invention, if adding these elements does not interfere with the formation of hydrogen-free nitrogen bridges. Network modifiers such as phosphorus, 20 alkali or earth alkali metals can also be added.

The refractive index of  $\text{SiO}_2$  is only to a minor extent affected by the presence of phosphorus. This is also expected for SiON with P. It was shown that the refractive index of silicon oxinitride correlates much stronger with the density of N-Si bonds. Hence phosphorus can here be used mainly for the reduction of losses while N can be used for the tuning of 25 the refractive index.

The described and claimed material can also be used as a gate isolator for MIS transistors. Here it replaces silica or silicon oxynitride. The advantage is that the material which is part of the invention contains more components than the presently used material. It may accommodate stresses or the structural mismatch at the interfaces towards silicon by changing its 30 composition locally. By accommodating a structural mismatch, unsaturated bonds at the

interface between a doped semiconductor and the isolator may be saturated with PSiON as the isolator, which otherwise may alter the electronic transport properties across the interface in undesired ways.

5 The tunable refractive index can also be used in an advantageous manner for window glasses or any other glass application with the glass being transparent at least partly in the infrared, the visible light spectrum and the near ultraviolet. The achievable glass has a higher refractive index than silica glass and a lower absorption than SiON in the infrared range.

PSiON can be made by mixing materials with weight ratios which result in the correct overall composition, e.g.  $\text{SiO}_2$ ,  $\text{Si}_3\text{N}_4$  and  $\text{P}_2\text{O}_5$  in powder form, heating it until the materials  
10 are fully mixed and reacted according to its stoichiometric conditions. PSiON can be made by a PECVD (Plasma enhanced chemical vapor deposition) process using an adequate combination of materials out of silane, nitrous oxide, ammonia, nitrogen gas and phosphine as precursor molecules. Other precursors providing for the involved elements are also conceivable. The material is solid, with other words at least temporarily stable or metastable  
15 and may be amorphous, polycrystalline or single crystalline. Any statement herein made for PSiON is also applicable for any material according to the formula  $\text{Si}_x\text{O}_y\text{N}_z\text{A}_2\text{M}_v\text{H}_u$ .

## CLAIMS

1. Material characterized in that it comprises essentially the composition  $\text{Si}_a\text{O}_x\text{N}_y\text{A}_z\text{M}_v\text{H}_u$ ,  
wherein  $a > 0$ ,  $x > 0$ ,  $y > 0$ ,  $v+z > 0$ ,  $u \geq 0$ , M is a chemical element of group 1 or 2,  
except H, or of group 11 or 12, and A is a chemical element of group 15 except N, or  
5 of group 16 except O.
2. Material according to claim 1, characterized in that  $z \geq y$  and/or  $v \geq y$ .
3. Material according to claim 1 or 2, characterized in that the refractive index n is  
approximately at least 0.1 larger than that of silica, preferably the silica usable in a  
cladding of a lightwaveguide.
- 10 4. Material according to one of claims 1 to 3, characterized in that  $v > 0$  and the atoms of  
the chemical element M are interstitially incorporated into the matrix of SiON.
5. Material according to one of claims 1 to 4, characterized in that the atoms of the  
chemical element M and/or atoms of the chemical element A effect the transformation  
of NH bridges into hydrogen-free bridges and/or avoidance of NH bridges.
- 15 6. Material characterized in that it comprises essentially SiON in which instead of one or  
several Si-atoms the respective number of atoms of a different element is incorporated  
and/or in which atoms of a different element are added, such that at least one  
hydrogen-free nitrogen bridge occurs.
7. Material according to claim 6, characterized in that by the different element at least one  
20 NH bridge is transformed into the hydrogen-free bridge.
8. Material according to claim 6 or 7, characterized in that the different element which is  
incorporated instead of Si is a chemical element of group 15 or 16 except N and O,  
and/or the different element which is added is a chemical element of group 1, 2, 11 or  
12, except H.
- 25 9. Material according to one of claims 1 to 8, characterized in that at least a part of the N  
atoms is coordinated to only two different atoms.

10. Material according to one of claims 1 to 9, characterized in that it has a structure similar to the structure of  $\text{SiO}_2$ .
11. Use of a material according to one of claims 1 to 10 as optical-waveguide material and/or as gate-isolating material and/or as transparent material.

1/3

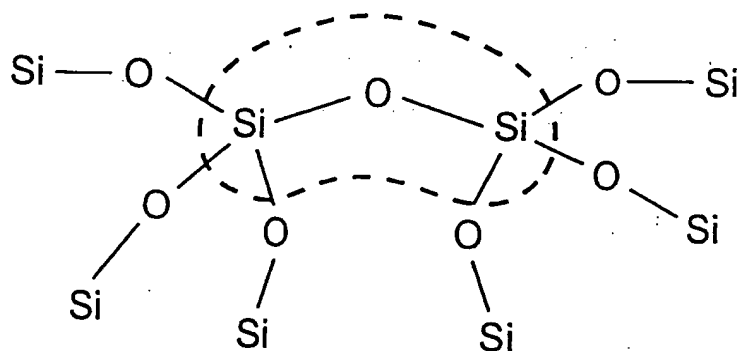


Fig. 1a

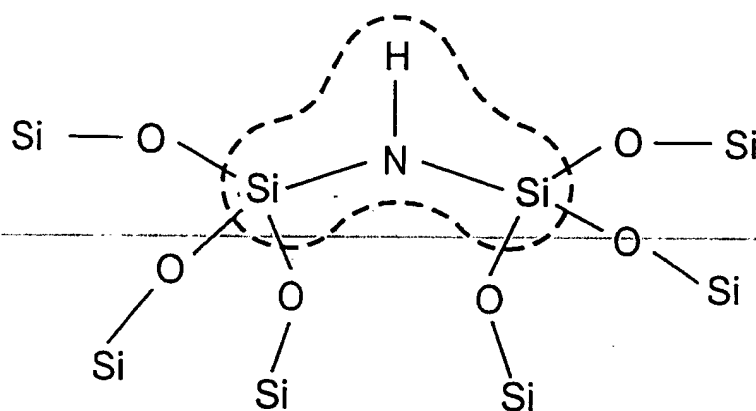


Fig. 1b

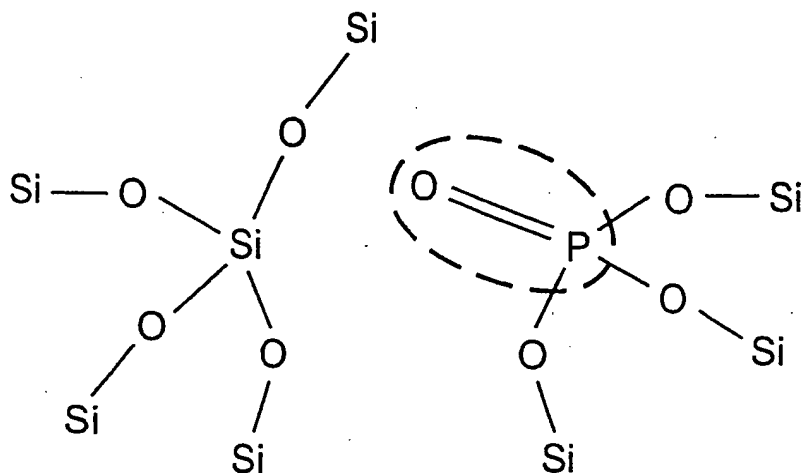


Fig. 1c



2/3

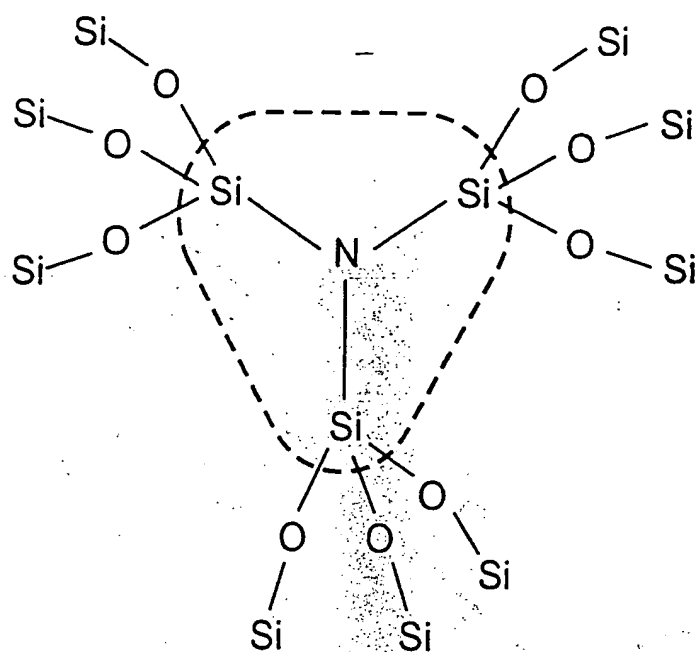


Fig. 1d

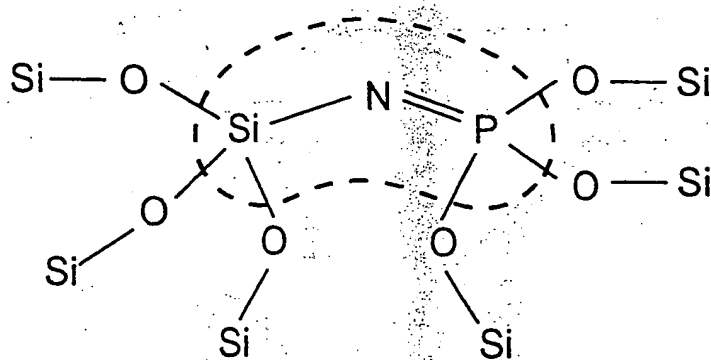


Fig. 1e

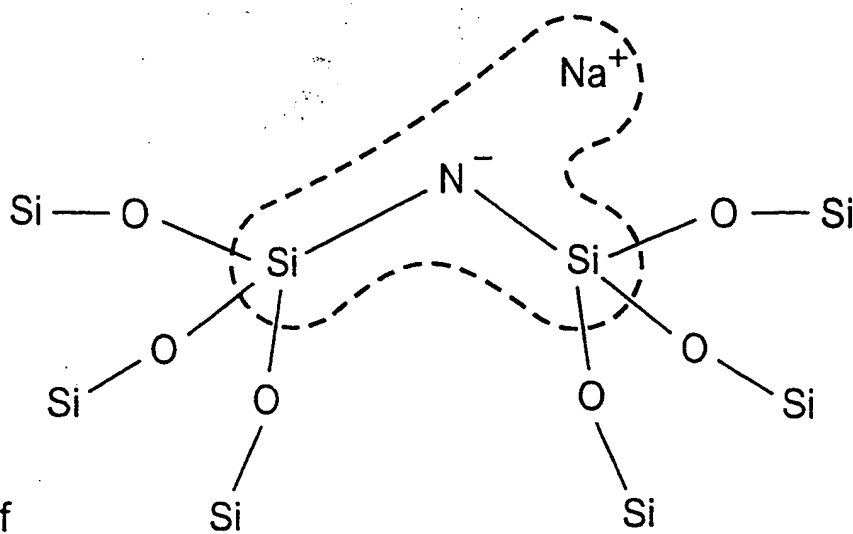


Fig. 1f

3/3

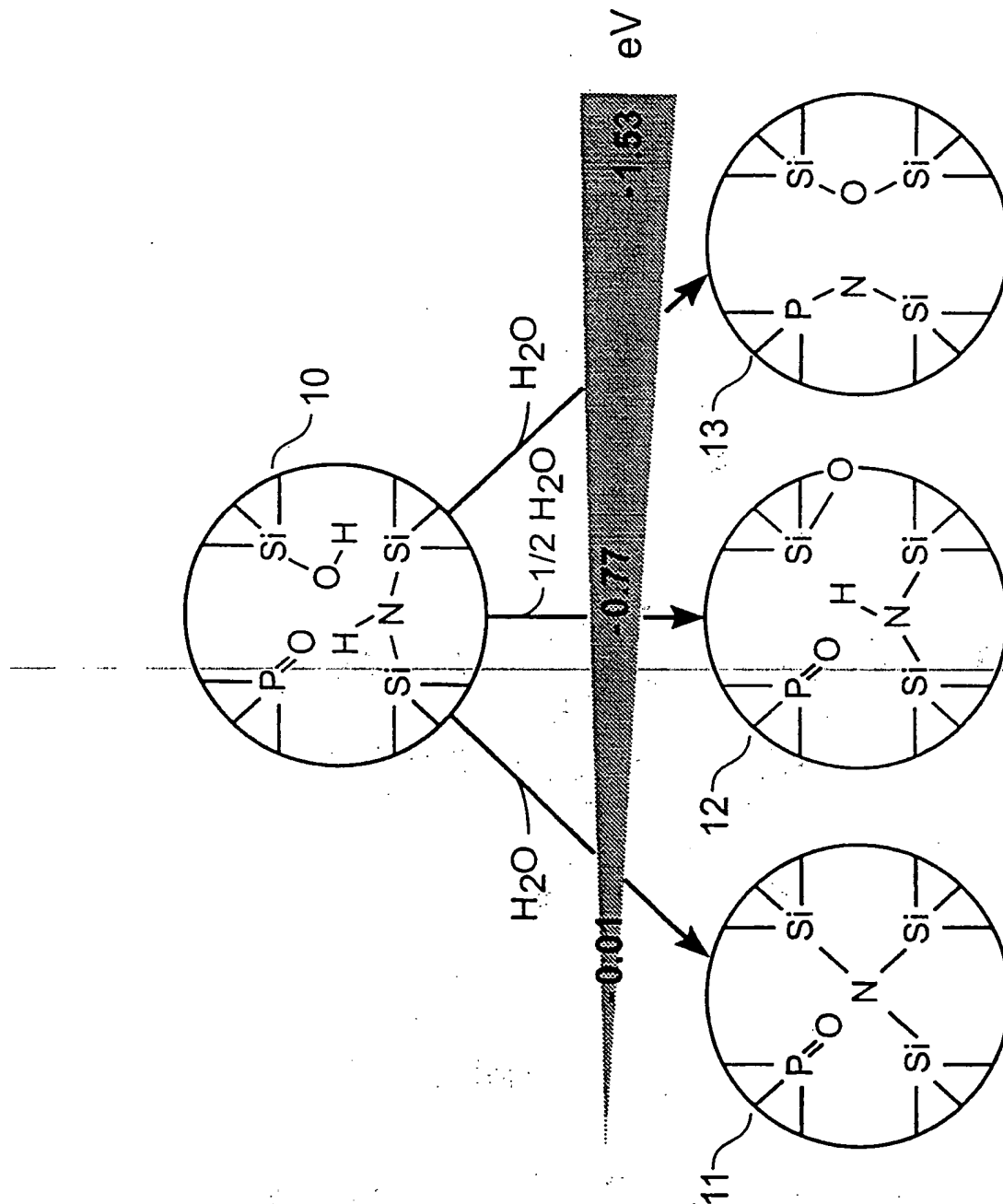


Fig. 2

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/IB 98/01017

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C01B21/082 C01B21/097 G02B6/00 H01L29/78

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C01B G02B H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	FR 2 526 001 A (CENTRE NAT RECH SCIENT) 4 November 1983 see the whole document	1
Y		11
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

17 November 1998

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## INTERNATIONAL SEARCH REPORT

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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